

Report No. IITRI-U6046-4
(Progress Report)

DEVELOPMENT OF A FLEXIBLE MATERIAL
RESISTANT TO NITROGEN TETROXIDE AND HYDRAZINE

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SCOPE

This report covers the work performed during the period of August 10 to September 6, 1966 on the "Development of a Flexible Material Resistant to Nitrogen Tetroxide and Hydrazine", Project U6046 under JPL Contract No. 951483.

The primary objectives of this program are to synthesize and evaluate selected fluorinated polymeric systems for utilization as materials of construction for the containment of nitrogen tetroxide and hydrazine-type fuels. The materials and products to be studied and evaluation tests to be carried out are specified in JPL Contract No. 951483.

WORK PERFORMED

Preparation of Thiocarbonyl Fluoride

Continued work on the synthesis of thiocarbonyl fluoride has involved the initial dimerization reaction of thiophosgene. Although our preliminary reactions gave low yields of the dimer under ultraviolet light irradiation, it was decided to study this reaction further since alternate methods of preparation of this carbonyl fluoride proved difficult also. During this report period we have investigated the dimerization of thiophosgene using selected sensitizers such as acetone, acetophenone and benzophenone. In addition, benzoyl peroxide was employed as a catalyst in one reaction to promote dimerization.

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In other experiments the use of carbon tetrachloride or chloroform as the reaction solvent has been investigated.

Dimerization experiments conducted in the presence of a sensitizer, either acetone, benzophenone or acetophenone, were not successful in producing greater yields of the desired dimer. Low yields of the dimer were obtained along with a substantial quantity of a heavy viscous oil from which the dimer was difficult to isolate. The dimer-oil ration was essentially the same regardless of experimental conditions employed.

The use of benzoyl peroxide as a catalyst for the dimerization of thiophosgene was examined in a single experiment. Results of this experiment were unrewarding in terms of an increased yield of the dimer utilizing 0.1% benzoyl peroxide.

More recent experiments employing carbon tetrachloride or chloroform as the solvent have been more successful in giving improved yields of the dimer. The thiophosgene-solvent ratio have yielded the dimer in greater quantity. In the present small scale reactions (7.5g) the dimer has been obtained in yields of 25-35% which is a significant improvement over previous results. The influence of reaction time on yield is presently being investigated.

Preparation of Polyanhydrides

Polymerization studies on perfluoroglutaric acid have been continued. These studies have involved the use of trifluoroacetic anhydride instead of acetic anhydride as the condensation reagent, and polymerization experiments conducted at lower temperatures in the usual manner.

Reactions involving the use of trifluoroacetic anhydride were not successful in yielding polymeric materials.

Polymerization of perfluoroglutaric acid (5.5g) to the polyanhydride using acetic anhydride was carried out at lower temperatures than previously employed. The prepolymerization step was conducted at reflux for 16 hours followed by polymerization under reduced pressure at 150-160 for 48 hours and 200°C for 16 hours. The product was separated into a semi-solid portion (0.3g) and a solid portion (2.65g). The solid portion was insoluble in acetone and displayed properties similar to the polymers prepared previously.

Further compatibility testing of the polyperfluoroglutaric anhydride with nitrogen tetroxide and hydrazine have shown that these materials are degraded to some extent. Testing was conducted by adding the polymer samples to tubes containing either nitrogen tetroxide or 95% hydrazine at temperatures of 0-5°C and 25-27°C, respectively. Over a period of three weeks, the nitrogen tetroxide had partially dissolved the polymer, and the remaining polymer particles were soft and spongy. Evaporation of the liquid N_2O_4 gave a solid residue. This change

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appeared to be one involving solubility rather than chemical attack. In contrast, hydrazine appeared to have dissolved the polymers to a greater extent while causing an increase in the extent of swelling of the particles. In these latter tests, it is thought that chemical attack of hydrazine on the anhydride linkages occurred since the recovered polymer was found to be soluble in solvents such as acetone, dioxane and dimethylformamide whereas the initial polymer was insoluble in these solvents.

Polymers From p-Hydroxybenzotrifluoride

Preliminary studies on the polymerization of p-hydroxylbenzotrifluoride have been carried out following techniques developed by Dow Chemical Company. Initial experimental efforts are directed toward the polymerization of this compound in diethylbenzene using sodium amide as catalyst. Polymerization conditions were 120°C for a period of 60 hours. The polymer was a pale yellow solid, being soluble in acetone and displaying carbonyl absorption in its infrared spectrum. Our initial compatibility tests of this polymer with nitrogen tetroxide and 95% hydrazine show that this material dissolves in both solvents over a period of several hours with some degree of discoloration.

Preparation of Octafluorotetrahydrofuran

The chlorination reaction involving 3,3,4,4-tetrafluoro-tetrahydrofuran, an intermediate in the synthesis of octafluoro-tetrahydrofuran was completed successfully and presently this product is being fluorinated to give the desired octafluoro-tetrahydrofuran.

FUTURE WORK

Preparation of Thiocarbonyl Fluoride

Emphasis in this area will be directed at scaling-up thiophosgene dimerization the reaction so that larger quantities of the dimer may be available for subsequent reactions leading to thiocarbonyl fluoride.

Polymerization of p-Hydroxybenzotrifluoride

Further work is planned in the polymerization of p-hydroxy-benzotrifluoride and in compatibility tests with N_2O_4 and hydrazine.

Polymerization of Octafluorotetrahydrofuran

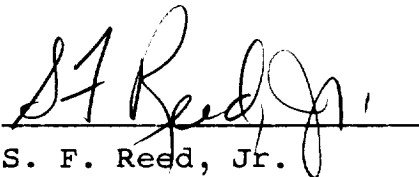
Initial polymerization studies will be conducted on completion of the final fluorination reaction.

PERSONNEL

The work was performed by Mr. Terry Yamauchi, Assistant Chemist, and S. F. Reed, Jr., Senior Scientist. The data are recorded in Logbook C17031. S. F. Reed, Jr. was on vacation for a two week period during the month of August.

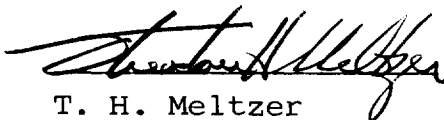
Respectfully submitted,

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